Spectroscopic Evidence For Interstellar Ice in Comet Hyakutake

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Volatile compounds in comets are the most pristine materials surviving from the time of formation of the Solar System, and thus potentially provide information about conditions that prevailed in the primitive solar nebula[1-3]. Moreover, comets may have supplied a substantial fraction of the volatiles on the terrestrial planets, perhaps including organic compounds that played a role in the origin of life on Earth[4-6]. Here we report the detection of hydrogen isocyanide (HNC) in comet Hyakutake. The abundance of HNC relative to hydrogen cyanide (HCN) is very similar to that observed in quiescent interstellar molecular clouds, and quite different from the equilibrium ratio expected in the outermost solar nebula, where comets are thought to form. Such a departure from equilibrium has long been considered a hallmark of gas-phase chemical processing in the interstellar medium[7], suggesting that interstellar gases have been incorporated into the comet's nucleus, perhaps as ices frozen onto interstellar grains. If this interpretation is correct, our results should provide constraints on the temperature of the solar nebula, and the subsequent chemical processes that occurred in the region where comets formed.

The identification of HNC was made in comet C/1996 B2 (Hyakutake) through its J=4-3 transition at 362.630092 GHz. The first detection was obtained at the James Clerk Maxwell Telescope (JCMT) on March 16.6 UT when the comet was at 1.219 AU from the Sun and 0.305 AU from the Earth. Observations quickly organized at the Caltech Submillimeter Observatory (CSO) on March 22.5, when the comet was closer to the Earth (0.137 AU), allowed confirmation of the line with a high signal-to-noise ratio. Both sets of hydrogen isocyanide (HNC) observations were preceded by measurement of the hydrogen cyanide (HCN) J=4-3 line at 354.505472 GHz, from which an abundance with respect to the principal volatile in the nucleus (water) of $HCN/H_2O \approx 0.0016$ may be estimated.[8] The pointing was monitored regularly using continuum sources (measured pointing shifts ≤3.5"), and the cometary ephemeris was checked by performing small maps of the HCN distribution. The spectra are shown in Figure 1; observed line intensities are given in Table 1.

Because the rotational constants and electric dipole moments of the closed-shell species HNC and HCN are very similar, the energy level populations for these two isomers are thought to be nearly equal when excitation is dominated by collisions (the situation in dense interstellar clouds[9,10]). This case should apply close to the nucleus in the cometary coma, so that the ratio of intensities observed for a given transition will closely approximate the ratio of abundances, apart from possible effects of optical depth for the more abundant species, HCN (these effects are not large; see Table 1 legend). The HNC/HCN abundance *ratio* is thus largely independent of assumptions that are necessary to calculate absolute molecular production rates, unless the distribution of these species in the inner coma is quite different (we return to this possibility in point 6 below). Farther from the nucleus the excitation will be dominated by the solar radiation field and fluorescence equilibrium may be approached[11]; however, this does not seem to be a major effect for the beam sizes employed here (Table 1 legend).

The ratio of the integrated areas (I) under the J=4-3 line profiles for HCN and HNC from the JCMT observations was $I(HNC)/I(HCN) = 0.074 \pm 0.015$, while the CSO observations on March 22 obtained $I(HNC)/I(HCN) = 0.092 \pm 0.014$. Correcting for optical depth (line saturation) of the HCN transition produces an abundance ratio HNC/HCN ≈ 0.06 on both dates. This value is approximately equal to the abundance ratio HNC/HCN found in interstellar clouds which have a kinetic temperature on the order of 50 K and is consistent with the upper limit of 0.3 which was found for Comet Halley[12,13]. In contrast, the chemical equilibrium ratio at 200 K, the expected near-nucleus coma temperature, is less than 10^{-15}, and is even less at lower temperatures[14]! As far as we can determine, the presence of a significant amount of HNC in a comet had not been predicted, presumably because the higher densities in the solar nebula relative to interstellar clouds would tend to drive the chemistry closer to equilibrium abundances. How may we account for the present observations? We consider several possibilities.

(1) The HNC may be surviving interstellar molecular material originally produced by gas-phase chemistry. In interstellar clouds the gas-phase abundance ratio HNC/HCN can exceed unity in cold (10 K) clouds; it also appears to exhibit a marked dependence on local kinetic temperature (T_k), with values decreasing to of order 0.005 for T_k Å 200 K [10,12,15]. A relatively high abundance ratio is predicted by the kinetics of gas-phase, ion-molecule chemistry, although a number of uncertainties remain concerning branching ratios of relevant reactions, the cause of the putative temperature dependence, and so on.[7,16,17,18]. Moreover, models suggest that the large gas-phase ratios can be retained as the molecules freeze out onto dust grains, although some decrease in the ratio might occur through processes in the grain mantles[19]. According to the model of Greenberg[20], cometary nuclei are agglomerates of largely unprocessed interstellar grains. The present HNC/HCN ratio is consistent with this model, if gas-phase HNC and HCN condensed onto such grains in the interior of the cloud which ultimately contracted to form the solar nebula, and then survived without isomerization, first in the grain mantles, then during the formation of the solar nebula and subsequently for the 4.5 Gyr lifetime of the Solar System, and finally during the processes associated with production of the cometary coma. Although neither HCN nor HNC has unequivocally been identified in the icy mantles of grains in dense interstellar clouds, such grains do exhibit an absorption feature at 4.62 micrometres which may arise from either nitriles or isonitriles ("XCN")[21,22].

(2) HNC might be produced by irradiation of an icy matrix containing HCN. This could conceivably occur either in the mantles of interstellar grains, in grains within the solar nebula, or near the surface of the cometary nucleus after its formation. Ultraviolet irradiation of HCN in an Argon matrix is known to produce HNC, and in fact was the technique used in early laboratory characterization of the HNC molecule[23]. If this mechanism were operative, it would imply the presence in cometary nuclei of the much more complex organics produced in laboratory irradiation of interstellar ice analogues[3,24]. However, ultraviolet and particle radiation should only penetrate the outer few micrometres to millimetres of the nuclear ices[2]. Thus, if irradiation of ices is the source of HNC, it would be much more effective before incorporation of interstellar grains into a cometary nucleus, because the entire grain mantle could then be subject to such processing. Thus, in this case the HNC would still probably be of interstellar origin.

(3) HNC might be produced by non-equilibrium chemical processes in the solar nebula itself, whatever the prior history of the nebular material. Various sources of energy are available, including ultraviolet photons, lightning, shock heating and solar flares.[25] Processes similar to those active in interstellar clouds might play a role. Existing models have not, to our knowledge, considered the production of HNC. In fact, some consider that HCN itself is probably surviving, unprocessed interstellar material rather than being a nebular product[2]. If the cometary HNC could be shown to have been produced in the outer solar nebula,

it might imply that other extreme departures from thermochemical equilibrium (such as the large hydrogen isotope fractionation observed in meteoritic organic matter[26]) might be the result of nebular rather than interstellar processes.

Finally, we must consider whether HNC might be produced in the cometary coma directly. There are various possible mechanisms.

(4) Could HNC be produced by gas-phase processes in a manner similar to that which occurs in the interstellar medium? At the nucleus of a typical comet at 1 AU from the Sun, the gas temperature and density are, respectively, about 200 K and 10^{13} cm^{-3}, several times and many orders of magnitude greater than the corresponding values in quiescent molecular clouds[27]. However, the rapid expansion in the coma leads, according to models, to a drop in temperature within several hudred kilometres of the nucleus to about 50 K, while the density decreases as the inverse square of the distance from the nucleus[27]. When the solar radiation field and the radiative and chemical effects of cometary grains are taken into account, the resulting chemistry becomes extremely complicated[28]. It may be that ions such as H_2O^+ and H_3O^+ produced by solar ultraviolet irradiation would charge transfer to HCN, leading to HCNH$^+$, which (as in the interstellar models) could undergo dissociative electron recombination to produce HNC, HCN and CN.

(5) The solar radiation field, which is of course absent in the interstellar case, might produce novel effects in the cometary environment. It has been calculated[29] that infrared relaxation of HCN from vibrational levels of the ground electronic state with more than about 2 ev of internal energy leads to an HNC/HCN ratio of about 0.05, essentially equal to our result. Radiative decay from the bent excited electronic states[30] of HCN would tend to populate these vibrational levels. Thus, if the cross-section for ultraviolet absorption by HCN to populate the excited electronic states were sufficiently large, the observed HNC might be the product of such photochemistry. Present indications, however, are that the rate of non-dissociative excitation of the electronic bands of HCN at 1 AU in the solar radiation field is much less than both the photodissociation rate and the infrared vibrational excitation rate, and hence probably not significant[11].

(6) A more familiar process in the coma for producing an unstable species such as HNC would be photodissociation of a heavier molecule; the radicals which dominate the optical spectra of comets are such "daughter species". The similar line shapes for HCN and HNC, resulting from Doppler broadening due to mass motion in the coma, argue against this possibility. We also note that, if HNC were a daughter product, its extended spatial distribution in the coma would lead to a calculated abundance much higher than that estimated here.

We consider that careful theoretical analysis, new laboratory experiments, and further astronomical observations will be necessary to sort out the implications of the present results. For example, careful modelling of coma chemistry for the deduced parameters appropriate to Comet Hyakutake should be carried out, in

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order to estimate an HNC/HCN ratio for varying compositions of the nuclear ices. Several questions may be subject to laboratory investigation: would HNC trapped in the nuclear H_2O matrix at ≤ 20 K survive isomerization to HCN during the 4.5-billion-year history of the Solar System? How much HNC is produced by irradiation of HCN in a water-ice matrix? Would HNC survive in H_2O ice heated to ~ 200 K as the comet approaches the Sun and the ices sublimate? Are the cross-sections for excitation of HCN to the excited electronic states indeed too low to be significant in the solar radiation field at 1 AU heliocentric distance? What are the dissociation cross-sections and branching ratios for possible parent molecules of putative daughter HNC in the coma? On the observational side, the current approach of Comet Hale-Bopp provides opportunities for seeking variations of the HNC/HCN ratio with both heliocentric distance and position in the coma, which would be expected if HNC is produced by photochemistry. Measurement of the DCN/HCN and DNC/DCN abundance ratios would allow comparison with interstellar values; both HCN and HNC can show deuterium enhancements of up to a factor of 1000 with respect to the cosmic D/H ratio[31]; a large deuterium fractionation would significantly strengthen the case for the survival of interstellar HCN and/or HNC in comets. Note that the HDO/H_2O ratio in Comet Halley is about twice the terrestrial value and an order of magnitude larger than the protosolar value, providing strong evidence for the survival of water from interstellar grain mantles[32] (the Comet Halley water ortho/para ratio also appears to support an interstellar origin[2]). HDO has been detected in Comet Hyakutake[33,34], but a firm determination of the D/H fractionation is premature at this time.

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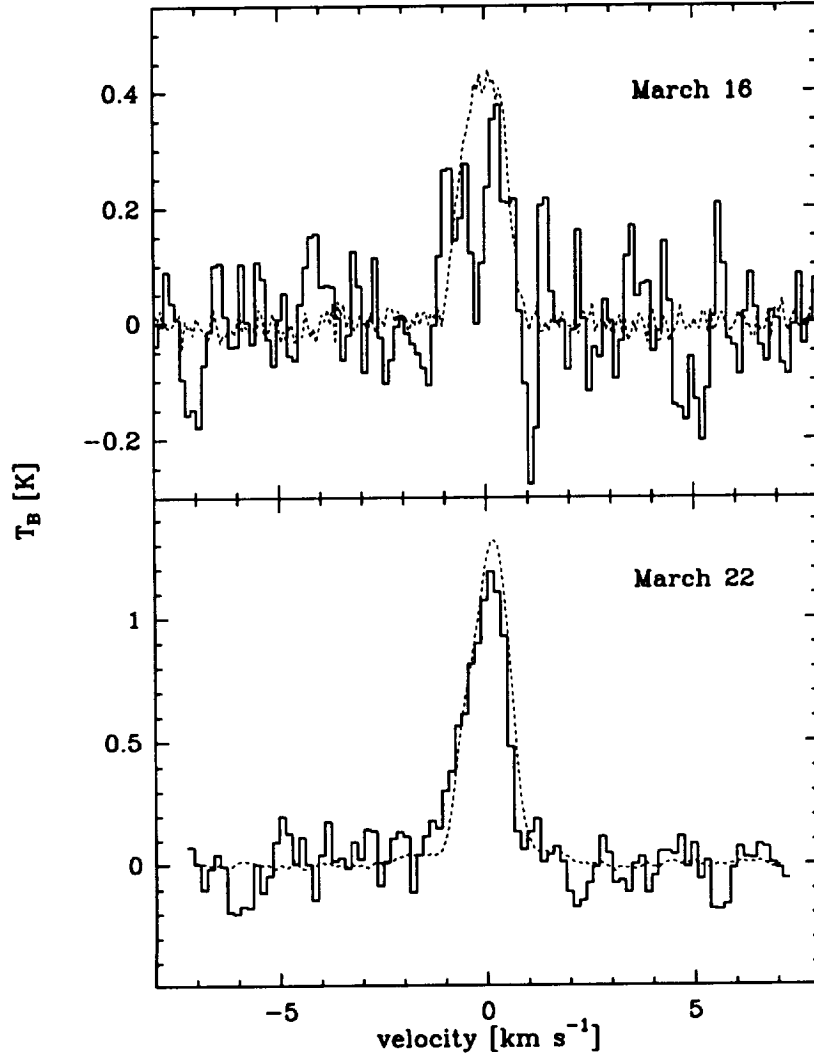35. Crovisier, J. *Astr. Astrophys. Suppl.* **68**, 223-258 (1987).

Figure 1: The J(4-3) line of hydrogen isocyanide (HNC; solid lines) and the corresponding J(4-3) line of HCN (dashed lines, spectra multiplied by 0.1) observed on March 16, 1996, at the James Clerk Maxwell Telescope (top) and on March 22, 1996, at the Caltech Submillimeter Observatory (bottom; see note to Table). The velocity scale is with respect to the nucleus. Spectral resolutions are 0.13 km s^{-1} and 0.16 km s^{-1} for the top and bottom spectra, respectively. The intensity scale is main beam brightness temperature.

TABLE 1   Parameters of the Observed Spectra

Date (UT)	r (AU)	Δ (AU)	Transition	Line Area (K km s^{-1})
JCMT	1.22	0.31		
March 16.50			HCN J=4-3	5.42 ± 0.07
March 16.63			HNC J=4-3	0.40 ± 0.06
CSO	1.10	0.14		
March 22.47			HCN J=4-3	16.47 ± 0.08
March 22.51			HNC J=4-3	1.51 ± 0.09

Notes: Observations toward presumed position of nucleus; intensity scale is main beam brightness temperature using efficiencies of 0.58 (JCMT) and 0.7 (CSO); r is heliocentric distance; Δ is geocentric distance; date is average during observation; integrated intensities computed over a 2 km s^{-1} velocity interval for the JCMT lines, and over 3 km s^{-1} and 5 km s^{-1} intervals for the CSO lines of HNC and HCN, respectively (the larger value employed to include all observed HCN hyperfine components). Quoted uncertainties do not include calibration uncertainties, estimated at 10%. For CSO observations Lis *et al.* (in preparation for *Asteroids, Comets, Meteors 1996*) estimate an optical depth of 0.7 at line center by comparing the strengths of the stronger to the weak hyperfine components of the HCN J=4-3 transition. This lowers the abundance ratio from the optically thin value of 0.09 to HNC/HCN ≈ 0.06. Opacity effects were probably less important at the time of the JCMT observations, owing to the larger area in the coma observed and the lower gas production and hence much lower column density; we estimate that the HNC/HCN abundance is indistinguishable from the later (CSO) value of 0.06. Another potentially complicating factor is the effect of radiative excitation and fluorescent decay in the solar radiation field, which will dominate collisional excitation in the outer coma. However, telescope beam sizes corresponded to only 2000 km (CSO) and 3000 km (JCMT) in the coma. Calculations with the HCN excitation model of Crovisier[35] show that most of the observed emission should have arisen from the collision-dominated region. The relative abundances of HNC and HCN should then not be overly complicated by effects of radiative excitation.